Reply to the “Comment on the publication ‘Ferroelectricity-free lead halide perovskites’ by Gomez et al.” by Colsmann et al.

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The existence of ferroelectricity in organic-inorganic perovskite thin films has been under debate over the past few years. If proven to exist, its magnitude in comparison to other known processes occurring in perovskite, such as electronic and ionic conductivities, will determine its importance for their optoelectronic properties. In a recent paper¹, our group aimed at contributing to the understanding of this topic by extending the range of measurements beyond what is conventionally carried out. In particular, we employed three techniques, namely, direct piezoelectric force microscopy, piezoelectric force microscopy, and electrostatic force microscopy, which we applied to two perovskite materials, prepared with control of film thickness and grain sizes that enabled the evaluation of morphological differences. Based on our experimental data, we concluded that lead halide perovskites are ferroelectricity-free.

This work prompted a comment² by the group of Prof. Colsmann (with manuscript ID: EE-CMT-12-2019-004159) in which the authors argued that the data that we presented were not conclusive to discriminate the existence or otherwise of ferroelectricity due to technical pitfalls. We genuinely appreciate the careful reading of our manuscript and the constructive criticism posed in the comment. In response, we intend first to clarify any technical aspect that might not have been sufficiently clear in the original manuscript. Then, we provide further experiments to show that the technical limitations that are claimed in the comment while might appear a priori reasoning, are in general, not supported by experimental evidence. Finally, we discuss the interpretation of our results in the broader sense, providing an explanation not only of the signals that we observe but also those found by a few other groups, data that have served to support the existence of ferroelectricity. Based on the literature as well as data we provide here, we find an explanation in terms of strain-compensation effects rather than ferroelectric domain formation a much plausible interpretation of their data. We thus maintain our conclusions: the thin films of the two perovskites that we studied are, for all practical means, ferroelectricity-free. In the interest of clarity, this comment is structured following the same order as the comments from Prof. Colsmann.

The first criticism considers the possibility that the measuring mode that we use will miss the generated charges for a fully in-plane oriented ferroelectric domain. As the authors of the comment mentioned, this argument holds only if the d_{31} piezoelectric tensor element is zero. Otherwise, even by working in vertical PFM mode, there will be a measurable signal despite the in-plane orientation of the ferroelectric domains. We agree that if the d_{31} piezoelectric tensor element for perovskites was zero, DPFM would also have difficulties to detect ferroelectricity. However, for all typical ferroelectric

perovskites, there is a non-zero d_{31} tensor component.³⁻⁵ In this respect, the existence of a piezoelectric material with d_{31} equal to zero would be exceptional and, if existent, it should be endorsed by proper measurements or references. Incidentally, vertical PFM images, similar to Colsmann et al. Lateral PFM pattern have been showed by other authors.^{6,7} Hence, if the perovskite would be the exceptional material with vanishing d_{31} tensor component, this would contradict their results. Or even worse, the data presented by A. Colsmann et al.^{8,9} would then correspond to a known artifact in PFM images, caused by the use of an extraordinarily soft and large cantilever tip, this is extremely prone to electrostatic interactions.

The second concern poses the question of whether our amplifier is really able to measure the weak signal expected from the perovskite samples, corresponding to a surface charge density of about $0.2 \mu\text{C}/\text{cm}^2$, and that we unfairly compared to PPLN ($78 \mu\text{C}/\text{cm}^2$) as a reference sample. We find this argument misleading. First, both DPFM and PFM measure the piezoelectric response of a material (in units of pC/N or pm/V) rather than any surface charge density.¹⁰ To estimate polarization charges, one should use a method called “nanoPUND”.¹¹ Note that the claims of the existence of ferroelectricity are not based on surface charge density, which besides not been conventional could easily result in artefacts due to ion migration, but rather on the measurement of the piezoelectric constant. In this respect, the d_{xx} piezoelectric constant -which is what a PFM or DPFM measurement yields- is very weak in PPLN ($6\text{-}16 \text{ pC}/\text{N}$). As illustrated by the d_{33} values listed in Table I below, PPLN exhibits the lowest piezoelectric constant among several known ferroelectric materials commercially available. This very low value was, in fact our motivation to choose lithium niobate as reference, as it represents an extreme case as compared to other typical piezoelectric materials, such as PMNT ($d_{33} = 2000 \text{ pC}/\text{N}$). Table I lists the d_{33} piezoelectric constant for representative examples.

Regarding the domain orientation of the reference sample, we do agree that having a reference with in-plane polarized ferroelectric domains would have been more convenient for comparison with perovskite films. Initially, we looked for such a sample but could not find any standard reference commercially available that we could use. So, we proceed to use samples with out-of-plane polarization and varying d_{33} piezoelectric constant values as references based on the fact that an in-plane polarization domain would exhibit a non-vanishing d_{31} piezoelectric tensor component. In any case, other authors have shown a similar domain structure as reported in the Vertical out-of-plane PFM.⁶

Table I: List of various ferroelectric materials and their characteristic piezoelectric tensor component d_{33} (literature sources included).

Material Name or Reference	d_{33} (pm/V or pC/N)	d_{31} (pm/V or pC/N)	Reference
PZT507	820	-360	Ref. ¹²
PZT5A2	375	-170	Ref. ¹²
PMNT	2420	1030	Ref. ¹³
PZNT	2400	2100	Ref. ¹³
Barium Titanate (BTO)	460	230	Ref. ¹⁴
BFO	16-60	-15	Ref. ¹⁵
Lead-Free NBT	110	-26	Ref. ¹⁶
Lithium niobate (PPLN)	6-16	6	Ref. ¹⁷

The third argument involves sample damage during the experiments. First, we note that the force is not what damages a sample during an AFM measurement. The ultimate variable that sets the threshold for damage is the *pressure* exerted by the tip. For instance, a couple of μNs applied through a single-crystal diamond tip with a radius of 5 nm would damage almost any hard material, due to the small tip-sample contact area. Our DPFM mode indeed needs to apply a higher force so the amplifier records the current levels generated, but, on the other hand, the tip-sample contact area is approximately a factor of 10 larger than the typical PFM measurements on oxides. We employ unconventional AFM cantilevers because these turned out to be especially suitable for measurements in DPFM mode due to an optimum balance between sensitivity and risk of causing damage. As a representative example, we show in **Figure 1a** below how a lithium niobate sample looks after intentional damage using a diamond tip. The plastic deformation caused by excessive pressure (not force) applied by the tip can be easily spotted. **Figure 1b-c** present several topography frames of subsequent scans on MAPbI₃ perovskite film. If the measurement by DPFM were damaging the sample, we should register a deformation in the topography channel during subsequent scans. However, it is not the case, as demonstrated in **Figure 1b-c**.

The fourth and last argument brought by the comments² states that we might lack sufficient spatial resolution to visualize the ferroelectric domains in the perovskite films. In our paper¹, we already provided experimental proof of an excellent spatial resolution by imaging the natural domain structure of a PZT5A4 ferroelectric sample, which exhibits tiny domains of 100 nm. For the case of the samples under study, **Figure 1d**) shows a 20x20 microns image of a MAPI sample with small dimension crystallites and sub-crystallite resolution. We found this test enough to prove our technique has sufficient spatial resolution. For instance, in the supplementary info we can see images with larger domains of up to 300 nm (**Figure S5**).¹⁸ Finally, we emphasize that this technique has been successfully applied to study, for example, ultra-thin films of BiFeO₃ (BFO), a genuinely ferroelectric material with a tiny domain structure.¹⁹

We next would like to make some general remarks about the existing experimental evidence against or supposedly in favour the existence of ferroelectricity in lead halide perovskite films, a controversy which, we now believe, is only apparent. We generally agree with the statement that not seeing a piezoresponse does not imply that there is no ferroelectricity. The critical point, which is simply ignored in the comment, is that we do see a DPFM signal. In the original paper, we not only demonstrate that this signal cannot be interpreted as due to the existence of ferroelectric domains, for it phenomenology disagrees with the behaviour of known ferroelectric materials, but also offer an explanation for its origin in terms of ion migration effects. As a consequence, we can further infer that if ferroelectricity existed in perovskites, its effects would be irrelevant for the photovoltaic performance, as compared to other phenomena like ion migration, structural instabilities, polaron formation, dynamic disorder induced by the A-site cations, etc., which dominate the piezoelectric response of the perovskite films.

Figure1: (a) Topography image obtained after the plastic deformation of a lithium niobate sample using a single crystal diamond tip with a small tip radius. (b) and (c) Topography images obtained of a MAPI film after subsequent scans applying the typical high force of DPFM. No plastic deformation is observed on the images, 8x8 micrometers and 12x12 micrometers. (d) DPFM image of a natural domain structure of a ferroelectric sample in which distinct ferroelectric domains are readily found, image 20 x 20 micrometres.

From a more fundamental perspective, however, we ask ourselves why insisting in the existence of ferroelectricity in lead halide perovskites even though there is no theoretical evidence to support it. On the contrary, ab-initio electronic structure and Car-Parrinello molecular dynamics simulations performed for several structural models of the prototype MAPbI_3 perovskite,²⁰ for example, conclude that it is improbable that ferroelectric order can be sustained at room temperature in perovskites. This is mainly the consequence of the strong interplay between the dynamical (orientational) disorder of the A-site cations and the structural variability of the inorganic cage, which hinders long-range ferroelectric order. We note that the calculations that are referred to in the comment² do not demonstrate ferroelectricity directly but, instead, are carried out assuming that if the observed domains by Colsmann and coworkers correspond to ferroelectricity they should have a poalrization of $0.2 \mu\text{C}/\text{cm}^2$,

While the signal that we observed in the DPFM was related to ion migration, we did not claim that that was the origin of all observed signals. In this respect, we would like to provide an alternative interpretation of the domain structures observed in the PFM measurements reported by Colsmann et al., Concretely, we are convinced that the information repeatedly measured in PFM by Colsmann et al. is real, i.e. they are not an artefact; they are just wrongly interpreted as being ferroelectric. In turn, we provide a more straightforward and, at the same time, a plausible explanation for this phenomenon: The formation of alternating twin domains with a perpendicular orientation of the c-axis in adjacent domains, which is triggered by a ubiquitous mechanism of strain compensation, when the nanocrystalline film cools down supported on a substrate, transforming from the cubic to the room-temperature tetragonal phase. Probably, the most compelling and unambiguous evidence for crystallographic twin domains in tetragonal MAPbI_3 is obtained using low-dose transmission electron

microscopy (TEM) and selected area electron diffraction (SAED).²¹ The domains observed in TEM are around 100-300 nm wide and disappear/reappear above/below the tetragonal-to-cubic phase transition temperature (approx. 57 °C) in a reversible process that often memorizes the scale and orientation of the domains. The tetragonal $I4/mcm$ room-temperature phase of MAPbI₃ is obtained from the cubic phase only by an alternating rotation of the corner-sharing PbI₆ octahedrons along the c-axis. This leads to a slight elongation of the unit cell in c-direction and its concomitant shrinkage in the a,b-plane. For the typical nanocrystal sizes and thicknesses of the polycrystalline MAPbI₃ thin films used in solar cells, which are supported on a substrate, a deformation as a whole of each nanocrystal, when transforming to the tetragonal phase, would be too costly in terms of elastic energy. Strain compensation spontaneously triggers the formation of nanoscale stripes which alternate elongation and shrinkage to cancel elastic strain at the length scales of the crystallites. Perovskite films show a dominant (110) texture with the c-axis of the crystal unit cell being widely oriented in-plane. As illustrated by the sketch in Figure 3 of the paper of Rothmann *et al.*²¹, the twinning structure proposed to understand the SAED patterns consists of a series of adjacent stripes with perpendicular c-axis orientation, as expected from the mentioned strain compensation mechanism. The reason for the observation of such twin domains also in PFM experiments of Colsmann et al. is the fact that the off-diagonal piezoelectric tensor components d_{12} and d_{13} of MAPbI₃ are different.

Finally, we would like to point to a very similar stripe-pattern formation phenomenon occurring in mm-large MAPbBr₃ single crystals at temperatures around 150 K, corresponding to the phase transformation from tetragonal to orthorhombic. As can be seen in the videos supplementing this reply, when the single crystal is cooled down below the phase transition temperature and becomes orthorhombic, a distinct pattern of stripes develops. The pattern disappears as fast as the sample is heated above the transition temperature. This stripe-pattern formation is thus completely reversible, precisely like that observed in TEM.²¹ In our case, though, the stripes are much bigger (tens of micrometres), so they can be found under an optical microscope, exhibiting a transparent texture. We also checked by Raman scattering that the orthorhombic crystal structure is present in adjacent stripes. Once more, strain compensation is at the origin of the stripe formation. This time, however, the transformation from tetragonal to orthorhombic also involves a deformation of the unit cell in the out-of-plane direction, thus, leading to the observed surface corrugation. In this way, we pointed to the conclusion that the domain structure observed in some PFM measurements is due to twinning driven by strain compensation rather than ferroelectricity. In the conclusion of this part, it is equally valid

that the lack of a measurable signal does not imply the absence of ferroelectricity, as the converse statement: the mere observation of domains is not necessarily evidence of ferroelectricity.

In summary, we have provided further evidence and arguments supporting our claim that if hybrid perovskite films exhibited measurable ferroelectricity, our DPFM measurements would have sufficient precision and resolution to measure them. Additionally, we propose a simpler and more plausible explanation based on strain compensation as the origin of the twin domains reported in the literature.

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